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Obscurants for Infrared Countermeasures III

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13. ABSTRACT (Maximum 200 words) This report describes recent results in the search for an effective obscurant material. The goal is to identify a material that has an infrared extinction comparable to or greater than that of brass but without its toxicity or negative environmental impact. Eighteen new materials were selected based on their having promising bulk optical properties as well as favorable particle size distributions or packing densities. Laboratory measurements of extinction were carried out for the powders using the NRL apparatus in which the materials are entrained in a flowing gas stream such that the mass loading and infrared transmission are determined simultaneously. Carbon black was found to be the best obscurant material of the possible alternatives to brass investigated in this laboratory. Its volume extinction coefficient is lower than that of brass (by a factor of 2-3), but if the relative toxicities are taken into account, it may be a preferable obscurant material.				
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EXECUTIVE SUMMARY

Mid-infrared obscurant materials are needed by the Navy as an important component in countermeasures to defend against heat-seeking, antiship missile (ASM) attack. There has been an ongoing effort to identify successful obscuring materials that not only exhibit extinction in the spectral regions of interest, the short (3-5 μm) and long (8-12 μm) IR bands, respectively, but that also satisfy other criteria concerning toxicity, environmental impact, deployment capabilities, and availability. Brass exhibits favorable obscuration properties but it is also highly toxic and environmentally detrimental. This work is aimed at finding an infrared obscurant material with extinction comparable or superior to that of brass but without its toxicity and environmental effects.

This report describes recent results from this laboratory in the ongoing search for a suitable infrared (IR) obscurant. New candidate materials were selected and then characterized by laboratory extinction measurements. The measurements were performed using the NRL apparatus in which dry powder samples are entrained into a flowing gas stream such that the sample mass loading can be determined and its extinction measured by Fourier transform infrared (FTIR) spectroscopy. Previous results in our effort toward finding a suitable obscurant to replace brass were reported previously in which the candidate obscurant materials boron nitride and boric acid were investigated and found to have extinction properties inferior to those of brass. Subsequent studies were conducted on various kinds of materials, including salts, semiconductors, and oxides. Of the materials tested, graphite with a nominal 2 μm average particle size was found to have the highest mass extinction coefficients (approximately 0.72 m^2/g in both spectral bands). In most applications the amount of obscurant that can be used is volume-limited. Although the mass extinction coefficient of graphite in both the short and long infrared bands is higher than that of brass, it has a substantially lower packing density so that the volume extinction coefficients are lower. However, the environmental and toxicological impact of graphite is much lower, so that it may be a better choice as an obscurant if these considerations are considered to be important.

In this study, other candidate obscurant materials were identified based on a number of criteria and their extinction coefficients were measured in our laboratory. The materials include several forms of iron oxide, for which previous numerical calculations predicted high extinction coefficients (Owrutsky et al. 1999). The experimental results are considerably lower than those predicted. In addition, metal oxides and semiconductors with small particle sizes (<5 μm) with promising optical constants and favorable packing densities were tested. Forms of carbon powders other than graphite were investigated in search of a material with a mass extinction comparable to graphite but with a higher packing density. As a result, another carbonaceous material, carbon black, was identified as the best of the new obscurant materials investigated.

OBSCURANTS FOR INFRARED COUNTERMEASURES III

INTRODUCTION

The next generations of antiship missiles (ASMs) are expected to incorporate more sophisticated seekers. Many will use focal plane arrays (to discriminate against point sources) and operate in several infrared bands (3-5 and 8-12 μm). This presents a greater challenge for countermeasures with respect to spectral balance and deployment capability. One approach to countermeasures that is being developed combines obscuration and decoy technologies with modern deployment capabilities such as unmanned airborne vehicles. The goal of obscuration countermeasures is to mask the thermal signature of a target (e.g., a ship) by deploying a material that has low infrared transmission between the seeker and the target. Brass has been identified as an effective obscurant material based on its infrared attenuation (Edwards et al. 1992; Hartman 1995) and it is currently used by the Army for this purpose. But it also has been well documented that brass has undesirable toxicological properties (Haley and Kurnas 1993; NRC 1999). The work reported here is the result of an effort to find an effective infrared obscuration material with extinction capabilities comparable to or better than brass but without the detrimental environmental impact. These obscuration materials will be an integral component of the NRL Vertically Launched Imaging Infrared Decoy Technologies (VLD) Program (Veracka 1999).

This report describes recent efforts that are a continuation of previous work on identifying suitable obscurant materials for infrared countermeasures, which is a combined computational and experimental approach. The previous work has been described in two previous NRL reports (Ladouceur et al. 1997; Owruksy et al. 1999) and a conference proceeding (Ladouceur et al. 1998). The original study (Ladouceur et al. 1997) focused on brass and two newly investigated materials, boric acid and boron nitride. The extinction coefficients were measured in the laboratory and neither of the two new materials had a high enough extinction to be useful. The initial report also describes the computational and experimental methods being used at NRL for investigating obscurant material candidates. This includes an explanation of the theory and methodology for numerical calculations to estimate powder extinction based on Mie scattering extinction as a function of particle size distribution and indices of refraction. The method assumes single scattering and that the particles are spheres. It does not include two-flux effects (in-scattering) and the implementation is based on algorithms by Dave (1968). The experimental approach to measuring extinction coefficients for powders is also described. Quantitative extinction measurements are challenging because it is difficult to measure the transmission of a gas-suspended dry powder under conditions in which the mass loading can be determined.

The second report (Owruksy et al. 1999) presents measured extinction coefficients for 10 other candidate materials. Promising results were found for some inorganic salts, for which the particle size was probably not optimum. Graphite was identified as the best obscurant material of those measured. It has higher mass extinction coefficients (in both the long and short bands) than brass but its volume extinction coefficients are somewhat lower due to its low packing density. It was also noted that the experimental results for graphite were in good agreement with those from Mie scattering calculations factoring in the measured particle size distribution. An analytical expression for scattering of spheres was used to estimate

the best particle size for extinction to guide the selection of powder size distribution. The calculations also reproduce the phenomenon observed experimentally that extinction is low on the short wavelength side of a relatively narrow absorption band, as demonstrated in the case of silicon carbide. This complicates selecting materials on the basis of an absorption band falling in the long band region. The apparatus designed and constructed at NRL for measuring powder extinction has also been used to investigate the near-IR extinction of titanium oxide (Ladouceur *et al.* 1999). Several samples with different size distributions were investigated. The results further illustrate the well-known result that the particle size distribution dramatically affects the extinction properties. The experimental methods and apparatus for measuring the extinction coefficients in this work on new candidate obscurant materials are the same as those described in these previous reports.

TECHNICAL APPROACH

Overview

The approach is similar to that described in our previous reports on searching for an effective obscurant material, a combined computational and experimental approach. An important step is establishing the criteria for assessing material obscuration effectiveness. In the present case most of the computational component has already been carried out and previously reported and is only discussed briefly here. This includes developing a method for assessing the best particle size for obscuration based on the radiation wavelength and material indices of refraction. It also includes the more specific numerical calculations of extinction based on Mie scattering, such as for iron oxide.

Establishing the obscuration criteria is important for selecting an effective obscuration material. While the most important property is extinction, it would also be advantageous if the material did not adversely affect the environment when deployed. This includes not only marine biota but the personnel and systems on the ship. In this regard, brass is very toxic and may also short electrical systems. The high toxicity of brass was reported some time ago by Haley and Kurnas (1993) and has been confirmed in a more recent and comprehensive study (NRC 1999). Graphite and titanium oxide are much less toxic as indicated by both sources. It is also relevant to determine which extinction coefficient(s) to consider for rating the materials. For the intended applications, volume extinction is more important than mass extinction since most deployment methods (by grenade or some other vehicle) are volume- rather than mass-limited. Furthermore, extinction in the long band is probably more important than in the short band since most of the ship's thermal signal is due to emission in the long band (and newer seekers are using long band detection). Therefore, the salient extinction coefficient and the one that is used in this report for evaluating material effectiveness is the long band, volume extinction coefficient.

In the present study, 18 candidate obscurant materials were selected and measured. The materials were selected for various reasons. A few materials, acetylene black and carbon black, are forms of carbon similar to graphite, which exhibited high extinction. The goal was to find a material with mass extinction similar to that of brass but high packing density so that the volume extinction would be higher than that of graphite. Most of the other materials, barium sulfate (a salt), metal oxides, silicon, and binary semiconductors, were selected because in addition to promising optical properties, they could be procured with small ($< 5 \mu\text{m}$) average particle sizes. Several forms of iron oxide were chosen because calculations reported previously (Owrutsky *et al.* 1999) indicated that iron oxide exhibits a high mass extinction coefficient. The mass extinction coefficients were measured in the flowing powder FTIR apparatus. The packing densities were also measured, and the volume extinction coefficients were determined from these measurements.

Background and Definitions

Only a very brief description is provided here for optical quantities and definitions pertinent to our discussion. Somewhat more detail can be found in our previous reports and, of course, more comprehensive treatments are provided in textbooks on light scattering (e.g., Bohren and Huffman 1983; van de Hulst, 1983). Extinction is analogous to absorption except that light can also be attenuated by scattering in the former case. When incident radiation I_0 traverses a pathlength L of a material of concentration c and extinction coefficient $\sigma(\lambda)$, the transmitted intensity is given by

$$I(\lambda) = I_0(\lambda) e^{-\sigma(\lambda)cL}, \quad (1)$$

which can easily be related to Beer's Law for extinction $E(\lambda)$,

$$E(\lambda) = -\log \left(\frac{I_0(\lambda)}{I(\lambda)} \right) = 2.303\sigma(\lambda)cL. \quad (2)$$

The definition of the extinction coefficient $\sigma(\lambda)$ depends on how the concentration is expressed. If c is a number density (particles/m³), $\sigma_{\text{ext}}(\lambda)$ is a (simple or direct) extinction cross section in units of area (m²); if c is a mass loading (g/m³), then the coefficient is a mass extinction coefficient $\sigma_m(\lambda)$ in units of m²/g. Alternatively, the volume extinction coefficient, $\sigma_v(\lambda)$ in m²/cc, is obtained when the mass loading is multiplied by the packing density ρ_p , i.e., $\sigma_v(\lambda) = \rho_p \sigma_m(\lambda)$. Another way to consider $\sigma_v(\lambda)$ is when the concentration is a volume loading or packing fraction.

The extinction coefficient σ is the sum of contributions from scattering σ_{sc} and absorption σ_{abs} ; $\sigma_m = \sigma_{\text{sc}} + \sigma_{\text{abs}}$. Mass extinction coefficients $\sigma_m(\lambda, r)$ depend on the wavelength of radiation, particle radius and its complex index of refraction. The (dimensionless) extinction efficiency Q_{ext} is the ratio of the extinction cross section ($\sigma_{\text{ext}}(\lambda, r)$ in cm²) to the particle area A : $\sigma_{\text{ext}}(\lambda)/A(r)$. The mass (volume) extinction coefficient is the extinction cross section divided by the mass (volume) of the particle, which can also be expressed in terms of the extinction efficiency,

$$\sigma_m(\lambda, r) = \frac{\sigma_{\text{ext}}(\lambda, r)}{\rho V} = \frac{1.5Q_{\text{ext}}(\lambda, r)}{\rho d}, \quad (3)$$

where V , d and ρ are the volume, diameter, and density of the particle.¹ Powders are commonly polydisperse and the cumulative mass extinction coefficient is the weighted average over the particle size distribution by mass n_m which can be expressed as

$$\sigma_m(\lambda) = \frac{\int \sigma_m(\lambda, r) n_m(r) dr}{\int n_m(r) dr}. \quad (4)$$

The extinction coefficient is the sum of scattering and absorption contributions and it depends on the complex index of refraction m , $m = n + ik$. n is the real part of m and it contributes to scattering while k is

¹ The mass extinction coefficient decreases linearly with particle size (and diameter). This is because the ratio of cross sectional area to volume is inversely proportional to d . Also, the best particle diameter for extinction is proportional to the wavelength (as indicated in Eq. (5) below), so that it is easier to realize high extinction at shorter wavelengths; the best extinction is higher at shorter wavelengths.

the imaginary part and it governs absorption. Excellent examples of how absorption and scattering contribute to extinction for various materials and different particle sizes and wavelengths can be found in the plots in Hoock and Sutherland (1993). Most of the materials being investigated are in the intermediate size regime (r close to λ), where (in the absence of narrow absorptions) the wavelength dependence of extinction is primarily determined by scattering and the magnitude is mediated by absorption (k).²

The extinction as a function of particle size and wavelength can be determined either by an explicit Mie scattering calculation (provided the optical constants are known) or estimated by an analytical equation that approximates the exact Mie theory. In the latter approach, the scattering efficiency Q_{ext} can be expressed for nonabsorbing spheres in a general and convenient way using the extinction equation (van de Hulst 1983, p. 176). This is cast in terms of the phase shift, $\Theta = 2x = 4\pi r(m-1)/\lambda$ (which is analogous to the size parameter, $x = 2\pi r/\lambda$). As demonstrated previously (Owrutsky et al. 1999), it is possible to determine the value of $\Theta(\text{max})$ that corresponds to the maximum Q_{ext} and thereby estimate the best particle size for scattering and probably for extinction under specific conditions of m (or n), λ , and d ,

$$d = \frac{0.75\lambda}{m - 1} \quad (5)$$

This result indicates that for a material with $m = 2$, favorable particle sizes for extinction in the middle of the short ($\lambda = 4 \mu\text{m}$) and long ($\lambda = 10 \mu\text{m}$) bands are $d = 3 \mu\text{m}$ and $d = 7.5 \mu\text{m}$, respectively. Most of the materials being tested have real indices of 2 or greater so the optimum particles are close to those quoted or somewhat smaller.

Materials Selected for Testing

Our approach to finding a suitable infrared obscuring material is to select candidates considered to be improvements in terms of particle size distribution or packing density on materials that were found to exhibit promising extinction in our previous studies. Calculations indicated that iron oxide should have a high extinction and the iron oxide material investigated earlier was found to exhibit moderately high extinction even though the particle size was measured to be larger than optimum.³ Moderately high extinction was also measured for some salts, such as monoammonium phosphate (MAP), even though the particles were again quite large. Therefore, an attempt was made to find salts with both smaller particles ($< 20 \mu\text{m}$) and absorption bands in the relevant infrared range. The only material found was a sample of barium sulfate. A supplier was found (Atlantic Equipment Engineers) capable of providing several metal oxides and semiconductors with a quoted particle size of $< 5 \mu\text{m}$. Many of the materials tested in this study were obtained from this vendor. As noted, there was interest in exploring other forms of carbon in addition to graphite with the intent of finding one with similar mass extinction and higher packing density. Acetylene black and carbon black were tested.

² In general, the relative importance of scattering and absorption on extinction depends on the ratio of particle size to the radiation wavelength. (It also depends on other things, such as specific values for k and n .) For example, very small particles ($r/\lambda \ll 1$) with some imaginary component of m (nonzero k) behave like molecules in which the extinction is dominated by absorption and does not depend on particle size. Large particles are dominated by scattering but are in the physical optics regime so the scattering efficiency Q is constant with particle size.

³ The results of particle size analysis from two particle size laboratories were inconsistent. Particle Characterization Laboratories determined the average mass radius to be $14 \mu\text{m}$ while those from Micromeritics indicated that the average was about $4 \mu\text{m}$.

EXPERIMENTAL

Extinction measurements for dry powders were performed on the apparatus constructed at NRL (Ladouceur et al. 1997). Only a brief outline of the instrument is given here since it has been described in detail previously. Figure 1 is a schematic diagram and photograph of the apparatus. An aerosol flow tube serves as the sample compartment for a Fourier transform infrared spectrometer (FTIR, Mattson Instruments, Cygnus 100) operating with an external detector. Powder is manually placed in the groove of a rotating platen equipped with a scraper, which controls the powder height in the groove and consequently the mass loading. The powder is introduced to the tube by a venturi nozzle (Air-Vac Engineering Co., Inc. model TD110H). It is mixed with a nitrogen gas flow directed up the tube (total flow = 42.5 LPM). The flow tube is 87 cm long and has an 11.4 cm inner diameter and is equipped with two purged sidearms 35 cm above the funnel that are used to attach NaCl windows (13 cm from the tube) for the IR beam of the FTIR to intersect the entrained powder. Spectra are recorded in single-beam mode in the 500-4000 cm^{-1} range; they are typically collected with 4 cm^{-1} resolution by averaging 16 scans. The absorbance is obtained using a background scan taken before the powder is fed into the apparatus. A scan after the run is also taken to avoid interferences from material deposited on the window or other residual transmission changes. Measurements are performed using 2-8 g of material, which is taken up in 0.5-2.0 minutes (20-80 L), and the typical range of mass loading is 40-120 g/m^3 . For most of the trials, a significant amount of the powder does not become entrained in the gas flow and collects in the (removable) cone in which the flow tube is mounted. This material is weighed and subtracted from the starting sample mass to determine the mass actually entrained in the gas stream. Previous work demonstrated that the mass extinction coefficients measured were not strongly affected by the mass loading within the range used in these studies.

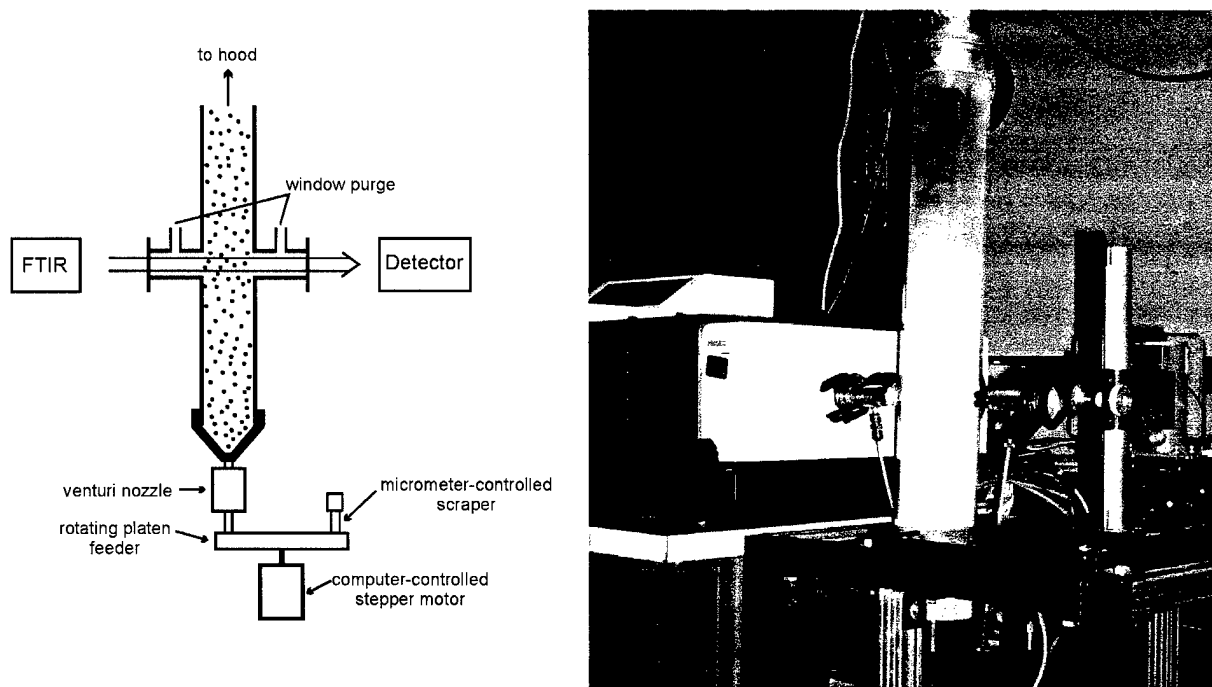


Fig. 1 — Schematic diagram of the apparatus used to measure extinction coefficients in this work (left); picture of the NRL powder flow - FTIR apparatus with titanium oxide flowing up the tube (right)

Packing densities are determined by placing approximately 5 ml of material in a 10-ml graduated cylinder and then tapping it down until there is no discernible change in volume (< 0.1 ml in 10 taps). The material in the cylinder is then weighed on a mass balance.

Most of the materials tested were obtained from Alfa Aesar⁴ and Atlantic Equipment Engineers. The materials from Alfa (with size description and catalog number) are acetylene carbon black (39724), aluminum oxide (gamma, 3 micron power; 39812), barium sulfate (1-4 micron powder; 13989), barium titanium oxide (< 2 micron powder; 88267), manganese titanium oxide (2 micron powder; 11398), manganese zirconium oxide (4 micron powder; 12343), and tin oxide (< 10 micron powder; 12283). The powders obtained from Atlantic Equipment Engineers are all quoted as having a < 5 micron particle size: tungsten carbide (WP-301), tungsten trioxide powder (WP-601), titanium carbide powder (TI-302), silicon powder (tech grade, SI-100), iron oxide black (FE-603), (magnetite) black (FE-602), hematite red (FE-601), yellow iron oxide (FE-605), antimony trioxide, (AN-601). Carbon black (BP3700) was obtained from Cabot Corporation. Manganese (IV) oxide (37,818-6) and copper (II) oxide (24,174-1; both < 5 micron powder) were obtained from Aldrich Co.

RESULTS: MEASURED EXTINCTION COEFFICIENTS FOR OBSCURANT CANDIDATES

The mass extinction coefficient is determined by the equation

$$\sigma_m = \frac{2.303A}{M_L L} \quad (6)$$

where A is the measured absorbance, L is the pathlength (which is the flow tube diameter for our measurements), and M_L is the mass loading, which is the mass of the sample divided by the total volume flowed. The factor 2.303 appears to convert the measured absorbance in common log to natural log for the calculation of σ_m (by which it is usually defined). Mass extinction coefficients $\sigma_m(\lambda)$ were determined over the range of 2-13 μm based upon the measured extinction spectra and sample loadings using Eq. (6). Volume extinction coefficients $\sigma_v(\lambda)$ were then derived by multiplying $\sigma_m(\lambda)$ by the measured tap density. Figures 2 and 3 show the measured volume extinction spectra for several of the materials investigated. Table 1 lists band-averaged mass extinction coefficients for all the new materials measured listed by decreasing long-band volume extinction. The table also includes packing densities for the powders as well as the relative rank by the other extinction coefficients (mass and short band volume). Figure 4 displays the extinction coefficients (mass and volume for both bands) in bar graph form. Table 2 is a cumulative list of all the materials tested at NRI, presented in a format similar to that of Table 1.

⁴ We appreciate the cooperation of Alfa Aesar who simplified the search for small particle size powders in their catalogue and inventory by providing a searchable list (in a text file) of their powder materials

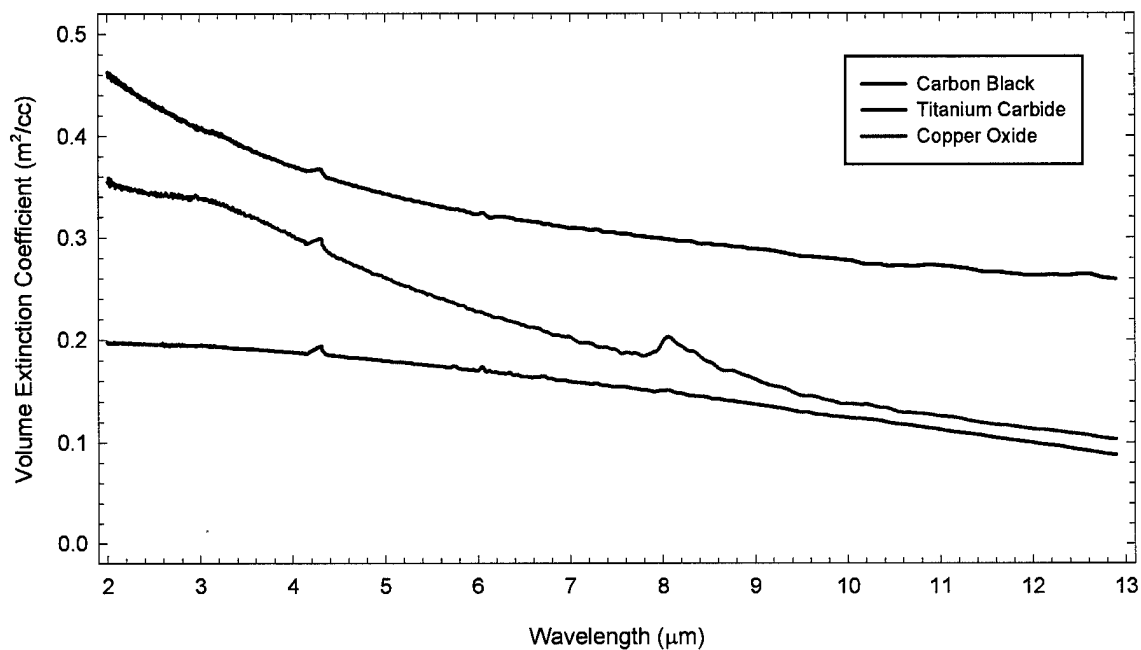


Fig. 2 — Volume extinction coefficients measured for carbon black, titanium carbide, and copper oxide

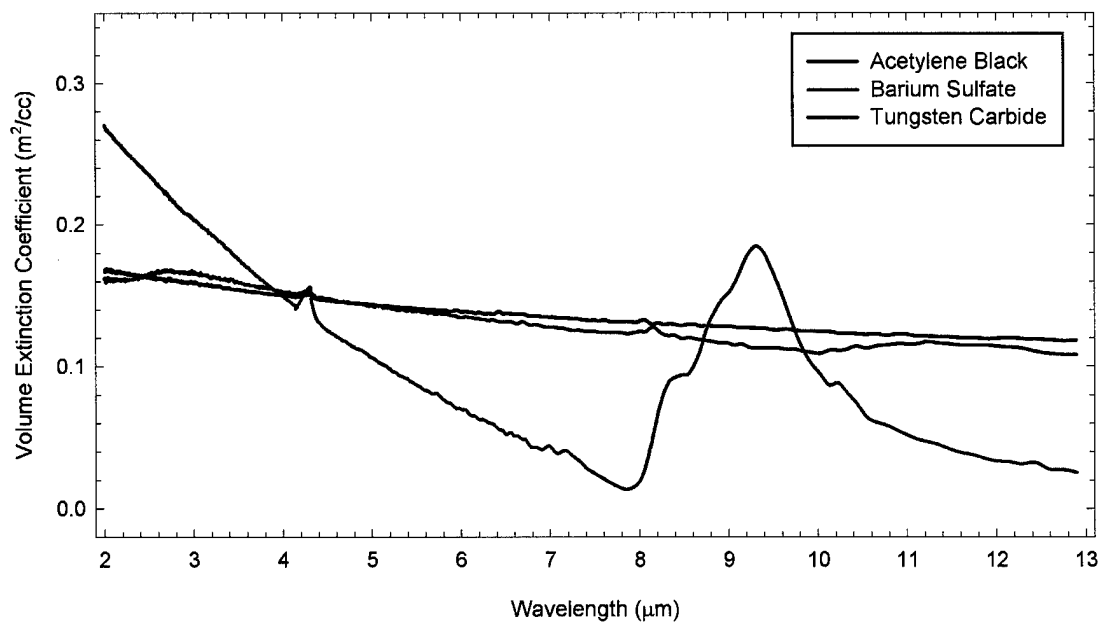


Fig. 3 — Volume extinction coefficients measured for acetylene black, barium sulfate, and tungsten carbide. Note the difference in the vertical scale compared to Fig. 2.

Table 1 — Extinction Coefficients of New Obscurant Materials Measured at NRL

	3-5 mass ext. coef.		8-12 mass ext. coef.		3-5 vol ext. coef.		8-12 vol. ext. coef.	tap density
	m ² /g	rank	m ² /g	rank	m ² /cc	rank	m ² /cc	g/cc
Carbon Black	0.83	1	0.62	1	0.38	1	0.29	0.46
Titanium Carbide	0.17	4	0.08	3	0.30	2	0.14	1.79
Copper Oxide	0.08	12	0.05	7	0.19	6	0.13	2.48
Acetylene Black	0.55	2	0.47	2	0.15	10	0.13	0.27
Tungsten Carbide	0.02	17	0.02	11	0.15	9	0.12	7.5
Barium Sulfate	0.09	10	0.05	6	0.16	8	0.10	1.88
Iron Black (Magnetite)	0.16	7	0.07	4	0.18	7	0.08	1.10
Manganese Oxide	0.19	3	0.07	5	0.21	5	0.07	1.10
Manganese Zirconium Oxide	0.08	11	0.03	9	0.13	11	0.04	1.58
Silicon	0.09	9	0.04	8	0.09	14	0.04	1.04
Manganese Titanium Oxide	0.17	6	0.02	13	0.23	4	0.02	1.36
Barium Titanium Oxide	0.17	5	0.02	12	0.23	3	0.02	1.36
Tungsten Oxide	0.01	18	0.01	18	0.04	16	0.02	3.12
Antimony Oxide	0.07	14	0.01	15	0.12	12	0.02	1.68
Tin Oxide	0.08	13	0.01	14	0.10	13	0.01	1.25
Iron Oxide (Red, Hematite)	0.04	16	0.01	16	0.04	17	0.01	1.07
Iron Oxide (Yellow)	0.10	8	0.02	10	0.05	15	0.01	0.51
Aluminum Oxide	0.05	15	0.01	17	0.03	18	0.01	0.68

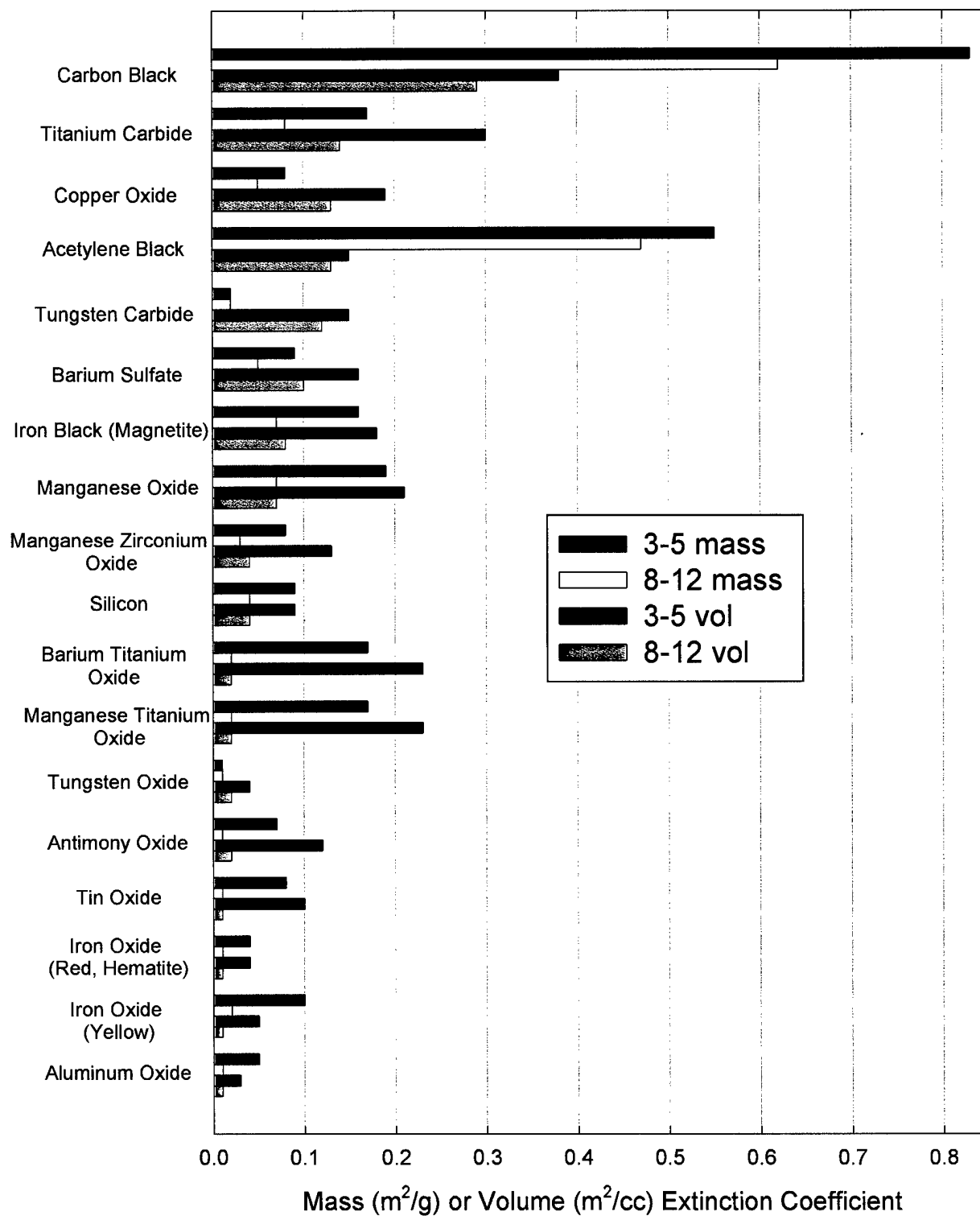


Fig. 4 — Bar chart of band-averaged mass and volume extinction coefficients for newly measured obscurant materials

Table 2 — Cumulative List of Obscurant Material Extinction Coefficients Measured at NRL

	3-5 mass ext. coef.		8-12 mass ext. coef.		3-5 vol ext. coef.		8-12 vol. ext. coef.	tap density	ref.
	m ² /g	rank	m ² /g	rank	m ² /cc	rank	m ² /cc	g/cc	
Brass	0.34	4	0.33	4	0.88	1	0.83	2.60	1
Carbon Black	0.83	1	0.62	2	0.38	2	0.29	0.46	3
Graphite (1-2)	0.74	2	0.73	1	0.21	8	0.21	0.39	2
Sodium Ammonium Hydrogen Phosphate	0.21	8	0.16	7	0.24	5	0.18	1.14	2
Graphite (-325 mesh)	0.23	6	0.24	5	0.17	13	0.18	0.74	2
Ammonium Hydrogen Carbonate	0.20	9	0.17	6	0.18	11	0.15	0.90	2
Titanium Carbide	0.17	12	0.08	11	0.30	3	0.14	1.79	3
MonoAmmonium Hydrogen Phosphate	0.22	7	0.11	10	0.27	4	0.14	1.20	2
Copper Oxide	0.08	24	0.05	18	0.19	10	0.13	2.48	3
Acetylene Black	0.55	3	0.47	3	0.15	18	0.13	0.27	3
Tungsten Carbide	0.02	32	0.02	24	0.15	17	0.12	7.50	3
Silicon Carbide 800 mesh	0.10	20	0.08	12	0.13	20	0.11	1.35	2
Glassy Carbon Spheres	0.11	18	0.13	8	0.09	25	0.10	0.79	2
Barium Sulfate	0.09	22	0.05	17	0.16	14	0.10	1.88	3
Iron Black (Magnetite)	0.16	14	0.07	13	0.18	12	0.08	1.10	3
Silicon Carbide 1200 mesh	0.12	17	0.07	14	0.14	19	0.08	1.12	2
Iron Black	0.24	5	0.11	9	0.16	15	0.08	0.67	2
Manganese Oxide	0.19	10	0.07	15	0.21	9	0.07	1.10	3
Titanium Oxide (visual fill)	0.13	15	0.06	16	0.16	16	0.07	1.10	2
Magnesium Zirconium Oxide	0.08	23	0.03	22	0.13	21	0.04	1.58	3
Silicon	0.09	21	0.04	21	0.09	24	0.04	1.04	3
Calcium Carbonate	0.12	16	0.05	19	0.09	26	0.04	0.79	2
Boron Nitride	0.07	27	0.05	20	0.05	28	0.03	0.67	1
Magnesium Titanium Oxide	0.17	11	0.02	25	0.23	6	0.02	1.36	3
Barium Titanium Oxide	0.17	13	0.02	26	0.23	7	0.02	1.36	3
Tungsten Oxide	0.01	33	0.01	33	0.04	29	0.02	3.12	3
Antimony Oxide	0.07	26	0.01	29	0.12	22	0.02	1.68	3
Tin Oxide	0.08	25	0.01	27	0.10	23	0.01	1.25	3
Boric Acid	0.02	31	0.01	28	0.01	33	0.01	0.67	1
Iron Oxide (Red, Hematite)	0.04	29	0.01	31	0.04	31	0.01	1.07	3
Iron Oxide (Yellow)	0.10	19	0.02	23	0.05	27	0.01	0.51	3
Aluminum Oxide	0.05	28	0.01	32	0.03	32	0.01	0.68	3

1. Ladouceur et al. 1997.
2. Owrutsky et al. 1999.
3. This work.

DISCUSSION

In this report we describe results of extinction measurements for several new obscurant material candidates. Powders were selected not only based on the materials' promising bulk optical constants or spectra, such as can be found in Palik (1984) and Nyquist and Kagel (1971), but also for their favorable particle size or packing density. In our previous study (Owrutsky et al. 1999), moderate mass extinction coefficients were measured for powders with relatively large (i.e., not optimal) particle sizes ($>15\text{ }\mu\text{m}$). Many had low packing densities that resulted in poor volume extinction coefficients. All the samples in this work have small particle sizes ($<10\text{ }\mu\text{m}$) that are closer to the optimum based on the scattering equation (Eq. (5)) for the range of material refractive index (2-3.5) and the spectral region of interest (3-12 μm). Some have high packing densities, several with $\rho > 2\text{ g/cc}$ and 7.5 g/cc for tungsten, which improves the likelihood for large volume extinction coefficients. We also tried to improve on our prior results for specific materials. Several varieties of iron oxide with small particle sizes were tested as well as a small particle size powder of a salt, barium sulfate. Graphite was the best obscurant material we found (especially based on mass extinction) of those from our earlier work. It had been demonstrated by other groups (Edwards et al, 1992; Hartman 1995)) that the mass extinction coefficients of graphite flakes are higher than those of brass flakes.⁵ It was also recognized that graphite has lower volume extinction coefficients compared to brass due to its much lower packing density. We examined other carbon materials (carbon black and acetylene black) to see if the mass extinction is sensitive to the morphology or specific form and to find a carbon material with comparable mass extinction and higher packing density than graphite, which would provide us with an effective obscurant material.

Based on volume extinction coefficients, none of the new obscurant materials tested exhibited better optical properties than brass, but carbon black was found to be an improvement upon graphite. Carbon black has the highest volume extinction coefficient in both bands ($0.38\text{ m}^2/\text{cc}$ in the short band; $0.29\text{ m}^2/\text{cc}$ in the long) of all the materials (other than brass) tested at NRL. These values are still 2-3 times lower than the NRL-measured values for brass (0.88 short, 0.83 long) and significantly higher than those for graphite (0.21 short, 0.21 long).⁶ While the extinction is almost the same in both bands for graphite, for carbon black it is about 30% higher in the short band. Since the wavelength for maximum extinction scales with particle size, this is consistent with carbon black being composed of smaller particles. The short-band mass extinction coefficient $\sigma_m(\text{SB})$ of carbon black is slightly higher than graphite, whereas in the long band it is higher for graphite. Although the carbon black packing density is low, it is still about 30% higher than for graphite, which accounts for the higher carbon black volume extinction in both bands. Acetylene black exhibits fairly highly mass extinction values; it has the third highest values overall in both bands, higher than brass and lower than both graphite and carbon black. But its volume extinction is lower (ranked $>10^{\text{th}}$ in both bands) because its packing density is even lower than graphite.

Among the other species investigated, titanium carbide, copper oxide, tungsten carbide, and barium sulfate have $\sigma_v(\text{LB})$ greater than $0.1\text{ m}^2/\text{g}$. Several of the materials reported previously have higher $\sigma_v(\text{LB})$ than all of these, including two salts, sodium ammonium hydrogen phosphate and ammonium hydrogen carbonate, as well as the larger particle size graphite (-325).⁷ Several powders recently tested

⁵ Our measurement of the graphite powder σ_m is about 3 times lower than those reported in Hartman (1995) and Edwards et al. (1992) for graphite flake. Similarly, our measured values for brass are also about three times lower than those listed in the same report. As we have noted previously, the relative σ_m are quite similar. The difference in the absolute values may be due to different morphology of the powders used or different deployment conditions.

⁶ The ratio of $\sigma_v(\text{brass})/\sigma_v(\text{carbon black})$ is 2 in the short band and 3 in the long, which is lower than that previously reported (by a factor of 6) for brass flakes and graphite flakes by Edwards et al. (1992).

⁷ For the graphite (-325) sample, the number refers to the sieve through which all the powder will pass (as indicated by the minus sign). In this report, the term "graphite" refers to the graphite 1-2 μm unless otherwise indicated.

have higher short band than long band volume extinction coefficients. Titanium carbide has the second highest $\sigma_v(\text{SB})$ after carbon black but its $\sigma_v(\text{LB})$ is lower by a factor of 2. Other materials have a very low $\sigma_v(\text{LB})$, such as manganese titanium oxide, barium titanium oxide, and manganese oxide. It could be that for these, the particle size is too small for good extinction in the long band. The salts measured previously also exhibit fairly high coefficients. No significant increase was realized for the small particle size barium sulfate sample. The barium sulfate optical properties may not be as good as the salts tested previously. A similar particle-sized sample of ammonium and phosphate or carbonate may yet provide a good obscurant.

We initially selected materials with at least moderately strong molecular vibrational absorption bands, such as for the salts and some semiconductors and metal oxides. This approach was initially reinforced by moderate early success with MAP. Some favorable results were obtained this way as can be seen in Table 2, in which 4 of the top 10 materials tested were salts. We had difficulty finding salts with small and narrow particle size distributions and the samples used are probably farther from being optimized in this respect than most of the other materials.

There is a drawback to searching for good obscurant materials based on (relatively narrow) absorption bands. These bands enhance extinction in the spectral region near the absorption maximum, but they also reduce (n , the real index of refraction, and as a consequence) scattering and extinction on the short wavelength edge of the band (Owrutsky et al. 1999). Therefore, absorption bands are most beneficial when they are situated on the short wavelength side of the spectral region of interest. Unfortunately, many species (silicon carbide, aluminum oxide, etc.) that absorb in the long band do so in the middle or on the long wavelength side of it (10-12 μm), so that with the scattering reduction, the absorption bands do not enhance the extinction. We initially thought it might be harder to find materials with good extinction in the short band compared to the long band since few molecules absorb strongly in the former. The data in the table indicate the opposite. There are only two samples (glassy carbon, graphite (-325)) for which the long-band extinction is higher. This could be because for a given particle, mass extinction scales inversely with wavelength.

Powder extinction depends on the particle size distribution, which may vary with the nature of the deployment. This complicates comparing extinction under different dissemination conditions.⁸ Laboratory extinction studies are useful to the extent that they correlate with results for field deployment. When particles are dispersed violently, such as with a screen cartridge in the field, they probably more closely approach the primary particle size and the best case extinction compared to when they are gently entrained as in the NRL apparatus. In the latter case, clumps are not broken up to the same extent, so that the extinction coefficients are probably underestimated (and possibly why ours are lower than in other reports). Therefore, countermeasure devices based on our measurements should provide the intended extinction, if not more. Another deployment-related property that is hard to predict but impacts obscurant performance is cloud persistence. A longer-lived cloud provides better time-integrated extinction.

Carbon black may be more susceptible to deployment conditions than most of the other materials. The primary particle sizes for carbon black are very small (<100 nm) but there is significant clumping to produce secondary particles, which probably dictate the scattering and affect the optical properties. The morphology of these species and how it affects the optical properties are complicated as described in a recent paper (Jäger et al. 1999). Since carbon black is composed of secondary particles that are loosely bound, a vigorous deployment of it (in the field) may result in a substantial extinction increase compared

⁸ Deployment or dispersion methods affecting the particle size distribution may also be an issue for other measurements used to characterize a powder. Distributions from laboratory particle size characterization results (e.g., some use liquid suspensions) may be different than those in our flowing apparatus or than those in the field. This may also contribute to some inconsistency in particle size distributions measured by different laboratories for the same sample

to the laboratory results if the particles are more broken up than in the gentler laboratory dissemination. Edwards et al. (1992) also noted that graphite sometimes ignited with their explosive deployment conditions. This tendency would probably be greater for carbon black.

One of the primary goals of this research is to find an obscurant material that provides extinction that is comparable to or better than that of brass. Brass provides good extinction but is highly toxic. We have identified carbon materials, graphite and carbon black, as the leading alternatives. It is relevant to consider the toxicity of brass and the alternatives, both in absolute and relative terms, and how to weigh material toxicity in considering the overall effectiveness or figure of merit for an obscurant material. A report by Haley and Kurnas (1993) indicated that brass is highly toxic. It was evaluated on a chemical scoring scale⁹ developed by O'Bryan and Ross (1988) to have the maximum toxicity rating of 9. Benign materials such as titanium oxide and Teflon were rated zero. Graphitic materials were found to have a toxicity about halfway in between with a rating of 3-4. Recent studies indicate, however, that graphite is only slightly more toxic than titanium oxide. A series of monographs (NRC 1997; 1999) have appeared in the last few years by the NRC Subcommittee for Military Smokes and Obscurants (of the Committee on Toxicology, NRC) which present comprehensive analyses of obscurant smoke toxicity. Recommended guidance exposure levels are given for military personnel and for military training facility boundaries. (The latter are 10 times lower.) The findings are similar to those from Haley and Kurnas (1993) with respect to the high toxicity of brass compared to titanium oxide, but the graphite levels are much closer to titanium oxide than to brass. One type of exposure level recommended by the NRC subcommittee is for 15 minute duration, military personnel, emergency exposure guidance levels (EEGL); in mg/m³, they are: titanium oxide, 1800; graphite, 880; brass, 1.6.¹⁰ Graphite is slightly (two times) worse than titanium oxide, based on the recommended guidance levels, but it is much better than brass; the level for graphite is 500 times lower than for brass. In their report, they recommend "that the Army's use of brass flakes be limited to minimize the potential for increasing toxicity with repeated exposures." There are no such warnings in the recommendations for the use of either titanium oxide or graphite flakes.

How should toxicity be incorporated into a combined figure of merit for obscurant material performance? An obscurant effectiveness (OE) index should probably include a minimum extinction coefficient criteria.¹¹ In order to consider materials (of the ones we have tested) other than brass, this would have to be at most than one-third the extinction of brass. The long band is a reasonable choice for which extinction coefficient to use, especially since it is almost always lower than for the short band. Currently, the best alternative material to brass, carbon black, has about three times lower volume extinction (two times in the short band). If we use the relative NRC guidance levels (GL) as the relative toxicity, then a simple product $OE = \sigma * GL$ places too much weight on the toxicity. (Assuming the GL for carbon black to be similar to that of graphite, its OE would be several hundred times higher than brass.) We propose an obscurant effectiveness defined as

$$OE = \sigma[(1 + \ln(RGL))] \quad , \quad (6)$$

where RGL is the relative toxicity based on the exposure guidance levels quoted above normalized by the lowest value, which is for brass. The RGL for material M is $GL(M)/GL(\text{brass})$ so that RGL values for brass, graphite, and titanium oxide are 1, 500, and 1130, respectively. The OE values determined this way

⁹ On this scale, as applied by Haley and Kurnas (1993), the EPA rating correlates with the exposure they report (in insects, EC_{50}) in manner that appears to be closer to a logarithmic than linear relationship.

¹⁰ Other levels are given for longer duration EEGL, in which the level scales inversely with time (i.e., same integrated dosage) and for repeated exposure (8hr/d, 5d/wk) which are approximately 1000 times lower than the 15-min EEGL. This book is available with online browsing from National Academy Press, <http://www.nap.edu>.

¹¹ The OE should also probably include the cloud persistence for the material to reflect time-integrated extinction, but we will leave it out since we do not have any information on this property for the materials.

are listed for several materials in Table 3. Some results are also given for salts, which we assumed to have the same toxicity of titanium oxide. The effect of including toxicity in the combined OE parameter yields results that are not surprising. The much higher toxicity and corresponding lower exposure guidance levels results in brass having the lowest OE for the materials listed except for the long band for titanium oxide. Carbon black has the highest OE for both bands. The next highest are MAP in the short band and graphite in the long band. If we include the constraint that any material considered as an alternative to brass must have a minimum extinction coefficient, $\sigma_v(\text{min})$, it would have to be no higher than one-third the value of brass ($\sigma_v(\text{min}) < \sigma_v(\text{brass})/3$) for carbon black to meet the criteria. If the minimum extinction coefficient were one-fourth of that of brass, graphite would qualify for the long band and sodium ammonium hydrogen phosphate and MAP would for the short band.

Table 3 — Obscuration Effectiveness from Extinction Coefficients and Toxicity for Several Materials

	Relative Exposure Guidance Level	3-5 volume		8-12 volume	
		ext. coeff. m^2/cc	OE	ext. coeff. m^2/cc	OE
Brass	1	0.88	0.88	0.83	0.83
Carbon Black	500	0.38	2.74	0.29	2.09
Graphite (1-2)	500	0.21	1.52	0.21	1.52
Sodium Ammonium Hydrogen Phosphate	1130	0.24	1.93	0.18	1.45
Graphite (-325 mesh)	500	0.17	1.23	0.18	1.30
Ammonium Hydrogen Carbonate	1130	0.18	1.45	0.15	1.20
MonoAmmonium Hydrogen Phosphate	1130	0.27	2.17	0.14	1.12
Acetylene Black	500	0.15	1.08	0.13	0.94
Titanium Oxide (visual fill)	1130	0.16	1.28	0.07	0.56

The most important result of this recent work is that the volume extinction for carbon black is somewhat higher than for graphite. Most of this appears to be from its higher packing density. The mass extinction is fairly similar for the various forms of carbon, which suggests an even more effective obscurant may be found by locating a form of carbon with a higher packing density.

SUMMARY

We have measured the IR mass and volume extinction coefficients for several powders as new obscurant candidate materials. Although the samples were chosen because their particle size distributions and packing densities appeared to favor higher coefficients than for those materials we measured before, none of them exhibited better extinction capabilities than brass. The best material, carbon black, was found to be somewhat better than graphite, which was our best alternative to date. A recent study (NRC, 1999) indicates that graphite is much less toxic than brass and closer to titanium oxide than indicated in a previous report. It appears that unless toxicity or some other factor is considered, brass remains the leading obscurant material in the infrared region.

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